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In Situ Growth of Aligned CdS Nanowire Arrays on Cd Foil and Their Optical and Field Emission Properties

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ABSTRACT

Aligned CdS nanowire arrays have been fabricated directly on a Cd foil via a simple solvothermal method. The metal Cd foil serves as both the Cd source and substrate during the fabrication of the aligned CdS nanowire arrays. The morphology, structure, and composition of the samples are characterized by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, and energy-dispersive spectroscopy. The aligned CdS nanowires are single-crystalline with a uniform diameter of 20-40 nm. The photoluminescence and Raman spectra disclose the optical properties of the products and the possible growth mechanism is proposed. The field emission properties are also investigated and analyzed. The screening effect is observed to play a vital role in the field emission properties due to the coalescent ends of the nanowires. The simple synthesis methodology in conjunction with the good field emission and optical properties make the materials both scientifically and technologically interesting.

I. INTRODUCTION

In recent years, well-aligned semiconductor nanowire and nanorod arrays have attracted increasing attention due to their unique properties and potential applications in novel optoelectronic nanodevices such as laser diodes, field emitters, solar cells, and sensors [1, 2]. Cadmium sulfide (CdS) is one of direct band II–VI semiconductors having a band gap of 2.4 eV. It is considered an excellent optoelectronic material and has important applications in nonlinear optical devices, flat panel displays, light emitting diodes, etc. [3, 4]. In the past few years, the synthesis, characterization, properties, and applications of one-dimensional (1D) CdS nanostructures have been extensively investigated. Various 1D CdS nanostructures and their arrays such as nanowires [5–7], nanorods [8], nanobelts [9], nanotubes [10] have been synthesized and some exciting properties have been revealed [11].

Field emission (FE), one of important applications of 1D nanomaterials, is of great scientific and commercial interest due to potential applications in flat-panel displays, microwave power amplifiers, traveling wave tubes, and other vacuum microelectronic devices. Research activities on 1D field emitters in the past decade have mainly focused on carbon nanotubes (CNTs) because of their high aspect ratio and small curvature radius, i.e. high field enhancement factor (β), as well as high mechanical stability and conductivity [12, 13]. Similar to CNTs, CdS nanowires or nanorods have small curvature radii, high aspect ratios, i.e. high β. Furthermore, CdS has a lower work function (4.2 eV) [6, 7] in comparison with CNTs (5 eV) [14]. Thus, CdS nanowires may be a good candidate as field emitters. Synthesis of well-aligned CdS nanowire or nanorod arrays is of particular interest for their good electrical and optoelectrical properties. Although 1D CdS nanowire or nanorod arrays have been synthesized by catalyst-assisted growth or the template-confined method [8], the use of templates or catalysts increases the complexity of the synthesis procedures and introduces some non-indigenous impurities that may influence their properties and even degrade their technological values.

In the work reported here, aligned CdS nanowire arrays were solvothermally synthesized in-situ on a Cd metal
foil in ethylenediamine without catalysts or templates. The as-synthesized CdS nanowires have uniform diameters of 20-40 nm and lengths up to micrometers. The Cd foil serves as both the substrate and Cd source to enable good intrinsic adhesion and electrical contact between the CdS nanowires and conducting Cd metal substrate, similar to our previous study on ZnO nanowires in-situ grown on a brass substrate [15]. Such a configuration is verified to yield good FE properties by this study. Furthermore, Raman and photoluminescence measurements indicate that the CdS nanowire arrays have good optical properties. The simple synthesis methodology together with the resulting good FE and optical properties make the materials scientifically and technologically interesting.

2. EXPERIMENTAL PROCEDURE

In a typical procedure, the pure cadmium foil (purity 99.9%) was first polished by an abrasive paper and then ultrasonically cleaned in acetone and distilled water sequentially. The solution was prepared by dissolving sulfur powders (S) in 30 mL ethylenediamine (en) which was stirred into a dark-green transparent solution. Afterwards, the solution was transferred to a Teflon-lined stainless steel autoclave and then the pre-treated cadmium foil was inunersed in the above solution. The autoclave was sealed and maintained at 160°C for 10 h. Afterwards, the autoclave was cooled to room temperature and the reacted cadmium foil was taken from the solution, rinsed with distilled water several times, and dried in vacuum at 60°C for 4h.

The morphology, structure, and composition of the as-synthesized materials were characterized by field emission scanning electron microscopy (FE-SEM, JSM 6335F), transmission electron microscopy (TEM, Philis CM20, 200 kV), high-resolution TEM (JEOL 2010F, 200 kV), X-ray diffraction (XRD, Siemens D-500), energy-dispersive X-ray spectrometry (EDS, Oxford INCA 200). XRD patterns were recorded using the graphite-monochromatized Cu Kα radiation (λ = 0.15406 nm) in the 2θ range of 20-80°. Before the TEM and HRTEM analyses, the CdS nanowires were carefully scraped off from the Cd foil and then strongly ultrasonically treated in ethanol for 30 min and then a drop of the solution was deposited on the Cu grids. Photoluminescence (PL) measurements were conducted at room temperature using the fourth harmonic of a Nd:yttrium-aluminum-garnet (Nd:YAG) laser with a wavelength of 244 nm the excitation source. The Raman spectra were obtained on T6400 and JY HR800 laser Raman spectrometers using the 514.6 nm line of an Ar+ laser as the excitation source. The field emission measurements were carried out using a parallel-plate diode configuration in a test chamber maintained at a pressure of 1.5 x 10⁻⁶ Torr.

3. RESULTS AND DISCUSSION

Figure 1 depicts the XRD pattern of the sample. All the diffraction peaks can be indexed to the hexagonal structure CdS (JCPDS card, No. 41-1049) with the exception of some Cd peaks (marked with asterisks) originating from the cadmium substrate. No impurity peaks such as elemental S can be detected. The intense (002) peak suggests that the as-prepared CdS nanostructures grow preferentially along the c-axis.

The general morphology of the sample is evaluated by SEM. The SEM images in FIG. 2 disclose that aligned nanowire arrays with coalescent ends are formed on the surface of the Cd foil. The high-magnification SEM image in FIG. 2(b) reveals that the uniform diameter of the isolated CdS nanowire is about 20-40 nm.

TEM and HRTEM are employed to further determine the structure and morphology of the product. The TEM image in FIG. 3(a) reveals that the nanowires retain the wire-like array geometry even after scraping off from the substrate and ultrasonic treatment for 30 min, suggesting that the as-grown nanowires have good alignment. The enlarged TEM image in FIG. 3(b) shows that the diameter of nanowires is about 35 nm, which is in agreement with the SEM results. The lower left and upper right corners of FIG. 3(b) present the SAED pattern and HRTEM image of an individual CdS nanowire, respectively. The spot pattern of the SAED...
image suggests that the nanowires are single crystal. The bright diffraction spots can be indexed to the (002), (101), (100) and (-101) planes of the wurtzite structure CdS. The interplanar distance calculated from the HRTEM image is about 0.336 nm, which corresponds to the \( d \)-spacing of the (002) planes of hexagonal CdS. It confirms that nanowires are single-crystalline with the growth direction of [001], also consistent with the XRD results. EDS spectrum in FIG. 3(c) shows strong Cd and S peaks and the atomic ratio of Cd/S is close to the expected stoichiometric ratio of 1:1.

**FIG. 2:** (a) Low magnification and (b) high magnification of SEM images of the product

**FIG. 3:** (a) and (b) TEM images and (c) EDS spectrum of CdS nanowire arrays. Insets of (b) are the ED pattern and HRTEM of an individual nanowire, respectively
According to our experimental observation, a possible formation mechanism is postulated. Under the solvothermal condition, the Cd foil can be easily activated by the strong nucleophilic nitrogen atoms of en to generate Cd atoms \([7, 16]\). At the same time, S dissolved in the en yields S species such as S\(^2\), S\(^{2-}\), S\(^{-}\) and other sulfur polyanions [17], which react with Cd atoms to form CdS nuclei. Partial CdS nuclei can be dissolved in the solution. When the reaction temperature is increased, the Cd\(^{2+}\) ions in the solution combine with the en molecule to form \([\text{Cd(en)}\nolimits_n]\)^{2+}, which reacts with S\(^{-}\) to form the CdS(en)_n complex. As the temperature is further increased, CdS(en)_n decomposes to generate CdS species. Afterwards, CdS nucleates on the surface of the Cd foil. In general, for the hexagonal wurtzite structure, the [001] is the fastest and preferential growth direction according to the growth kinetics [18, 19]. Thus, the CdS nuclei grow preferentially along the [001] direction to form 1D nanowires while growth on other directions are retarded. Consequently, aligned nanowire arrays are formed on the substrate.

PL and Raman spectra are acquired to determine the optical properties of the product. Figure 4 shows the room temperature PL spectrum of the as-prepared CdS nanowire arrays with 244 nm excitation. The results show one weak green emission band at about 550 nm and three strong emission bands at about 690 nm, 746 nm and 807 nm. The weak emission at 550 nm may be attributed to radiative recombination of e\(^-\) - h\(^+\) pairs at trap sites such as surface sulfide vacancies [20, 21]. The emission at 690 nm comes from trap or surface states [22] whereas the band at 746 nm may be ascribed to trap emission due to more surface and subsurface defects of the CdS nanowires [20, 23]. The emission band at 807 nm may arise from a certain concentration of intrinsic defects [24]. Figure 5 displays the Raman spectrum of the CdS nanowire arrays. The peaks at 301, 602, 905 cm\(^{-1}\) correspond to the first-order, second-order, and third-order longitudinal optical (LO) phonon modes of CdS, respectively [23, 25, 26].

FE measurements are performed to study the electron emission property of the CdS nanowire arrays on the Cd foil. It is carried out using a parallel-plate diode configuration in a test chamber maintained at 1.5 \times 10^{-6} Torr. The Cd foil covered with CdS nanowire arrays is used as the FE cathodes. A stainless steel electrode plate is used as an anode with a sample to anode distance of 100 \(\mu\)m. The Keithley 248 supplies the applied voltage and measures the emission current.

Figure 5 shows the current density \((J)\) as a function of the applied electric field \((E)\). From the \(J-E\) plot (FIG. 6), the turn-on field \((E_{\text{on}})\) (defined as an electric field to produce a current density of 10 \(\mu\)A/cm\(^2\)) is about 13.4 V/\(\mu\)m. The FE current-voltage characteristics are further analyzed by the Fowler-Nordheim (F-N) equation [27].
4.2 eV for CdS [6, 7]. In contrast to CdS nanowire arrays reported by other researchers [6, 7], the $\beta$ value of our CdS nanowire arrays is relatively lower, resulting in a little higher $E_{\text{to}}$. This may be ascribed to the large screening effect and less emitter tips due to the coalescent ends of the nanowires. Considering the screening effect between adjacent emitters, the field enhancement factor $\gamma$ of the emitter films can be expressed according to the Filip’s model as follows [28, 29]:

$$\beta = 1 + s(d/r - 1) \equiv 1 + s(d/r)$$

where $r$ is the radius of the emitter, $d$ is the average spacing between the electrodes, and $s$ is a parameter describing the degree of the screening effect valued from 0 for very densely arranged emitters to 1 for a single one. Substituting the $d$ value of 100 $\mu$m into our measurements and the average $r$ value of about 30 nm for CdS nanowires as $s = 1$, the theoretic enhancement factor $\beta$ can be estimated to be about 3334 from equation (2). For the actual $\beta$ value of 820 from our measurements, the screening effect parameter $s$ can be calculated to be about 0.246, which is similar to non well-aligned ZnO nanorods with the $s$ value of 0.177 reported previously [30].

4. CONCLUSION

CdS nanowire arrays have been synthesized in situ on a Cd substrate by the simple solvo-thermal method. The CdS nanowires have diameters of 20-40 nm and lengths up to micrometers. The possible growth mechanism is proposed. The PL and Raman measurements demonstrate good optical properties of the CdS nanowire arrays. Investigation of the FE characteristics indicates that the as-prepared CdS nanowire arrays grown on the metallic Cd foil exhibit good electron emission properties. The turn-on field is about 13.4 V/$\mu$m and field enhancement factor is 820. Theoretical calculation reveals that the screening effect due to the coalescent ends of the nanowires plays an important role in the FE properties of the sample. The simple synthesis methodology together with the resulting good FE and optical properties make the study scientifically and technologically interesting.

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